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SINGLET→TRIPLET ABSORPTION IN FROZEN *p*-BROMOTOLUENE

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ABSTRACT. The absorption spectra in the near ultraviolet region of a frozen transparent mass of *p*-bromotoluene of thickness 7.0 mm and of a frozen 12% solution of the compound in methyl cyclohexane at −180°C of thickness 45 mm have been investigated. In each case three sharp bands at 4045 A, 3812 A and 3603 A have been observed. By comparing this spectrum with the luminescence spectrum of the substance at −180°C it has been shown that in absorption the transition from the ground singlet state to the triplet state coupled to an excited vibration state is predominant and that the data lead to the values 1590 cm^{-1} and 1516 cm^{-1} respectively for the ground state and triplet state vibration frequencies of the molecule. It is pointed out that in the luminescence spectrum of the substance at −40°C the 0,0 transition is absent and that the vibration mentioned above is coupled to the transition in the luminescence.

INTRODUCTION

It was observed by Sanyal (1953) while studying the Raman spectra of ortho- and para-chlorotoluene that these compounds in the solid state at −180°C produce strong luminescence bands in the visible region. Biswas (1956a, 1956b) repeated the investigation and also extended it to ortho— and para-bromotoluene, using mainly the 3650 A group of mercury lines as the exciting radiation. He observed a large number of bands in each case, but the separation of successive bands could not explained satisfactorily by him. He further showed (Biswas, 1958) that the luminescence is actually an afterglow of short duration. Later, Roy (1959) showed that the luminescence of *p*-chlorotoluene disappears when the wavelength of the exciting radiation becomes greater than 3750A. It was, therefore, concluded that the luminescence was produced by absorption of radiation by transition from the singlet to the triplet state and then by re-emission of the absorbed energy. He further tried to find out whether there was discrete absorption bands in the near ultraviolet region in the absorption spectra of these compounds in the liquid state and observed (Roy, 1960) that in the liquid state *m*-fluorotoluene, *p*-chlorotoluene and *o*-bromotoluene show only continuous absorption on the longer wavelength side of the region near 3300A, where the absorption in benzene is very weak and that the region of absorption shifts towards longer wavelengths as the atomic weight of the substituent halogen atom

increases. In order to find out whether this continuous absorption was a property of the liquid state of the compounds Sirkar and Roy (1960) studied the absorption spectra of benzene and *o*-bromotoluene in the vapour state with a path length of 18.90 metres at pressures of about 120 mm and 55 mm of Hg respectively and in the liquid state having equivalent path lengths. They observed that even in the vapour state with a path length equivalent to 7 mm of the liquid, *o*-bromotoluene exhibits continuous absorption in the region from 3400 A to 3500 A and that the strength of this absorption due to an equivalent thickness of the liquid is much larger than that in the vapour. Benzene on the other hand shows very little absorption in this region and not much difference is observed between the spectra due to the liquid and equivalent path length of the vapour. Roy (1961) observed similar continuous absorption in this region in the case of almost all the isomeric monohalogen-substituted toluenes in the liquid and vapour states.

As already mentioned, the luminescence spectra of all the halogen substituted toluenes in the solid state at −180°C consist of bands while the liquids show continuous absorption in the region on the longer wavelength side of 3400 A. It can be inferred that the substances in the solid state at low temperatures might exhibit discrete absorption bands instead of continuous absorption in the region mentioned above As the absorption is extremely weak, a thick layer is to be used to study such absorption and it is difficult to obtain transparent thick layers of the substances in the frozen state. In the present investigation an attempt was made to obtain thick transparent masses of para bromotoluene both in the crystalline state and in the frozen solution in methyl cyclohexane and to study the absorption spectra in the near ultraviolet region. The results are discussed in the following sections.

EXPERIMENTAL

The liquid of pure quality supplied by B.D.H of London was further purified by distillation under reduced pressure. The solvent methyl cyclohexane was supplied by Fisher Scientific Co. of U.S.A. and it was also purified similarly. A nearly transparent frozen mass of *p*-bromotoluene at −15°C was obtained in a Pyrex glass cell of special design and having a thickness of 7 mm by cooling the liquid contained in the cell slowly from its lower portions. The method was similar to that for obtaining metallic crystals, the only difference being that in the temperature. This method was used when it had been found that the frozen mass obtained by immersing the cell in liquid oxygen was completely opaque. A 12 percent solution of the substance in methyl cyclohexane in a Pyrex glass glass cell of thickness 45 mm was held in a brass frame. When the lower portion of the frame was immersed in liquid oxygen contained in a transparent Dewar vessel the solution was frozen and a transluscent mass at about −175°C was obtained. The absorption spectra of these two solid masses were photographed using a hydrogen tube as the source of continuum and an

Adam Hilger E 1 quartz spectrograph giving a dispersion of about 10 A/mm in the region of 3500 A. Iron arc comparison spectrum was photographed on each of the spectrograms After drawing a sharp line along the line 4191 A of the iron arc spectrum with a razor blade and producing it to cut across the absorption spectrum, microphotometric records of the two spectra on each spectrogram were taken. The wavelengths on the absorption spectrum at any point was determined by finding the distance of the point from the mark due to the line 4191 A and the corresponding wave-length on the record due to the iron arc spectrum.

RESULTS AND DISCUSSION

The microphotometric records due to the spectrograms are reproduced in Figs. 1(a) and 1(b). It can be seen from the records that there are at least three sharp absorption peaks in the spectra due to both the pure crystal and the

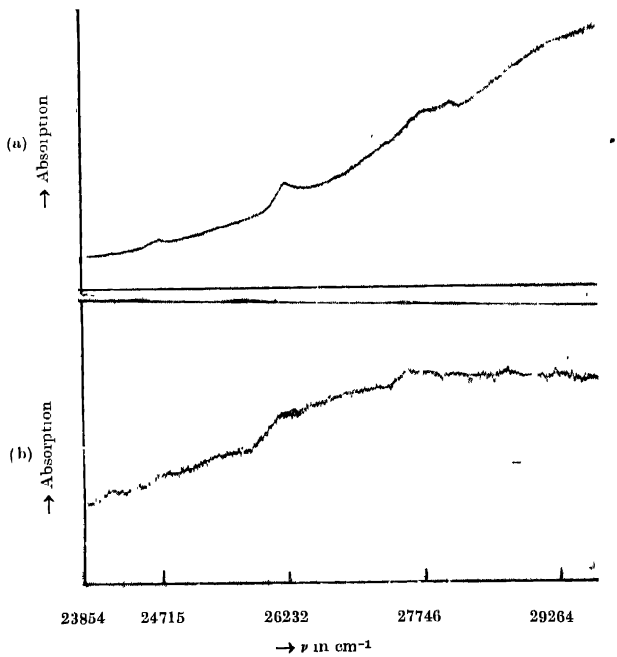

Fig. 1. Microphotometric records of absorption spectra.

(a) *p*-bromotoluene at −15°C.

(b) Solid solution of *p*-bromotoluene in methyl cyclohexane at −180°C.

frozen mixture. The wave numbers and strength of the absorption are given in Table I. A broad fourth band is also included.

TABLE I

Absorption bands of thick layer of *p*-bromotoluene

Pure crystals at −15°C		12% frozen solution in methyl cyclohexane at −180°C	
Positions	Separation	Positions	Separation
24715 m	—	24715 w	
	1517	—	1517
26232 s			
—	1514	26232 s	—
27746 mb	—		1514
	1518	27746 mb	—
29264 wb	—		

It can be seen from Table I that both the pure crystal and the frozen solution show absorption peaks of the same wavelengths and that the second peak is the strongest in each case. It is found that the mean separation between the successive bands is about 1516 cm^{-1}. This represents the frequency of some mode of vibration of the molecule in the triplet state. In order to identify the mode the luminescence spectrum of the compound reported by Biswas (1956c) is to be compared with the absorption spectrum. It is found that he observed a separation of 1717 cm^{-1} between the first two broad luminescence bands on the shorter wavelength side and the first band is at 4337 A, i.e., at 23051 cm^{-1}. The first absorption band observed in the present investigation, however, is at 24715 cm^{-1}. If the latter band be identified with the 0, 0 band in the singlet→triplet transition it is found that the 0, 0 band is absent in the luminescence spectrum. Denoting the vibration frequencies in the singlet and triplet states by ν_S and ν_T respectively, we assume athat the first band in the luminescence spectrum on the shorter wavelength side is due to a transition from the first excited vibrational state coupled to the triplet state to the second excited vibrational state in the singlet state of the molecule as shown in Fig. 2.

Then we get

$$2\nu_S - \nu_T = 1664$$

or $2\nu_S - 1517 = 1664$

or $\nu_S = 1590\ cm^{-1}$.

This agrees with the frequency of mode 8A of benzene (Pitzer and Scott, 1943).

The second band in the fluorescence spectrum reproduced by Biswas (1956c) is at 4686 A, but it is very wide and its strongest portion seems to be at about

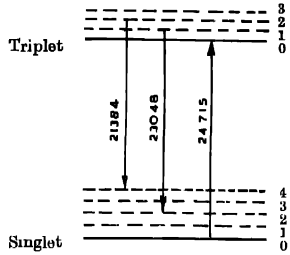

Fig 2. Schematic energy level diagram showing transitions between the Triplet→Singlet states.

4675 A, which is at a distance of 1667 cm^{-1} from the first band. This may be due to the transition from the second excited vibrational state in the triplet state to the fourth excited vibrational state in the singlet state. The transition from the first excited upper vibrational state to the third lower excited vibrational state would give a band at a distance of 1590 cm^{-1} from the band at 23051 cm^{-1} and there seems to be some intensity in this region in the luminescence spectrum reproduced by Biswas (1956c). Thus, the luminescence bands are broadened by the superposition of the different raansitions mentioned above. For an accurate analysis of the luminescence spectrum using the triplet state vibrational frequency found in the present investigation, a careful study of the structure of the luminescence bands is necessary.

It is thus concluded that somehow the mode No. 8A is responsible for the re-emission of the energy absorbed by singlet→triplet absorption which seems to be feebly allowed in the case of halogen substituted toluenes.

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